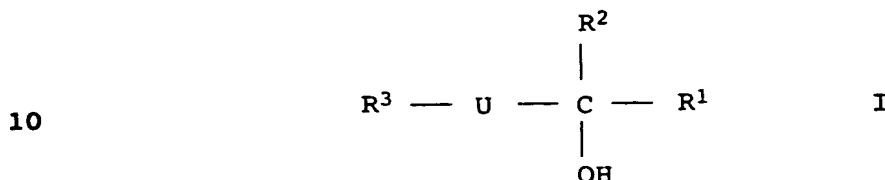


Preparation of α -oxidized carbonyl compounds

The present invention relates to a process for the preparation of
 5 a compound of the general formula I

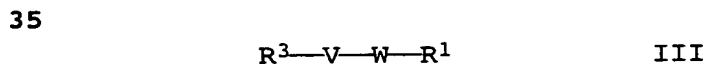


where R^1 , R^2 , R^3 are hydrogen, C_1 - to C_{20} -alkyl, C_2 - to
 15 C_{20} -alkenyl, C_2 - to C_{20} -alkynyl, C_3 - to C_{12} -cycloalkyl, C_4 - to
 C_{20} -cycloalkyl-alkyl, C_1 - to C_{20} -hydroxyalkyl, or aryl or C_7 - to
 C_{20} -arylalkyl which is unsubstituted or substituted by C_1 - to
 C_8 -alkyl, C_1 - to C_8 -alkoxy, halogen, C_1 - to C_4 -haloalkyl, C_1 - to
 C_4 -haloalkoxy, phenyl, phenoxy, halophenyl, halophenoxy, carboxyl,
 20 C_2 - to C_8 -alkoxycarbonyl or cyano, or R^1 and R^2 or R^3 together are
 a C_2 - to C_9 -alkanediyl unit which is unsubstituted,
 monosubstituted or disubstituted by C_1 - to C_8 -alkyl, C_1 - to
 C_8 -alkoxy and/or halogen and in which one or two methyl groups may
 also be replaced by a $(\text{CH}=\text{CH})$ unit and R^3 is additionally an
 25 acetylated carbonyl group in which the alkoxy groups are derived
 from an alcohol of the general formula II



30 where R^4 is C_1 - to C_6 -alkyl, and

U is an acetylated carbonyl group in which the alkoxy groups are
 derived from an alcohol of the general formula II, or
 is a compound of the general formula III



where R^1 is as defined under the formula I, and R^3 is
 exclusively aryl which is unsubstituted or substituted by C_1 -
 40 to C_8 -alkyl, C_1 - to C_8 -alkoxy, halogen, C_1 - to C_4 -haloalkyl,
 C_1 - to C_4 -haloalkoxy, phenyl, phenoxy, halophenyl,
 halophenoxy, carboxyl, C_2 - to C_8 -alkoxycarbonyl or cyano,

V is a carbonyl group or is as defined for U under the formula
 45 I, and

2

W is as defined for V, with the proviso that one of the groups V and W is a carbonyl group and the other is an acetylated carbonyl group,

5 or

a compound of the general formula IV

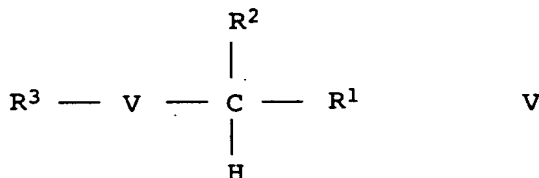


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where R^4 is as defined under the formula II, V and W are as defined under the formula II, and R^3 is as defined under the formula III,

15 by subjecting a compound of the general formula V

20



where V, R^1 , R^2 and R^3 are as defined under the formula I or III, 25 with the proviso that

- in the case where a compound of the formula III is desired, use is only made of a compound Va in which

30 R^1 is exclusively hydrogen and

R^3 is exclusively aryl which is unsubstituted or substituted by C_1 - to C_8 -alkyl, C_1 - to C_8 -alkoxy, halogen, C_1 - to C_4 -haloalkyl, C_1 - to C_4 -haloalkoxy, phenyl, phenoxy, 35 halophenyl, halophenoxy, carboxyl, C_2 - to C_8 -alkoxycarbonyl or cyano, and

- in the case where a compound of the formula IV is desired, use is only made of a compound Vb in which

40

R^1 and R^2 are exclusively hydrogen,

R^3 is exclusively aryl which is unsubstituted or substituted by C_1 - to C_8 -alkyl, C_1 - to C_8 -alkoxy, halogen, C_1 - to C_4 -haloalkyl, C_1 - to C_4 -haloalkoxy, phenyl, phenoxy, 45

halophenyl, halophenoxy, carboxyl, C₂- to C₈-alkoxycarbonyl or cyano,

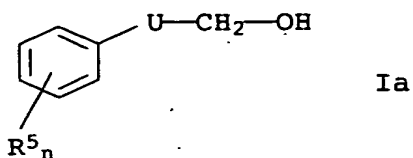
to an electrochemical reaction with an alcohol of the general
5 formula II in the presence of an auxiliary electrolyte and
catalytic amounts of a metal salt (S) derived from a metal from
the 1st, 2nd, 6th or 8th sub-group or from lead, tin or rhenium.

- Sub B2/
- EP-A-460 451 discloses a process for the preparation of
10 α -hydroxymethyl ketals by electrochemical oxidation of aldehydes
or ketones in the presence of alcohols and halogen compounds as
auxiliary electrolytes. Repetition of the examples shows that
more highly oxidized carbonyl compounds are also formed under the
process conditions described if the carbonyl group is in the
15 α -position to an aromatic radical. Thus, for example, a methylene
group in the α -position to the carbonyl group can be oxidized to
the carbonyl function and in addition the aldehyde or keto
carbonyl group originally present can be oxidized to the carboxyl
group. Thus, it is not only α -hydroxyketals that are formed, but
20 also α -ketaldehydes, α -ketoacetals, α -ketalcarboxylic esters and
 α -keto orthoesters. However, this process is still not entirely
satisfactory since the overall yield of these target products is
relatively low and in addition large amounts of other
substantially unusable products are formed.
25 German Patent Application 19904929, which is not a prior
publication, relates to a process for the preparation of
2,2,3,3-tetramethoxypropanol by electrochemical oxidation of
methylglyoxal dimethyl acetal using a mixture comprising
30 methanol, water and an auxiliary electrolyte as electrolysis
medium and an iron, steel, platinum or zinc cathode.

It is an object of the present invention to provide an
electrochemical process by means of which α -hydroxyketals,
35 α -ketalaldehydes, α -ketoacetals, α -ketalcarboxylic esters and
 α -keto orthoesters can be prepared from keto or aldehyde carbonyl
compounds. We have found that this object is achieved by the
process defined above.

- 40 The process according to the invention is particularly suitable
for the preparation of compounds of the general formulae I, III
and IV, where the radical R⁴ in the acetylated carbonyl group is
derived from methanol or ethanol.
45 Of the compounds of the formula I, preference is given to those
of the formula Ia

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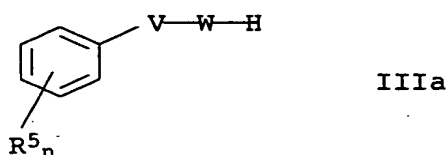


where U is as defined in formula I,

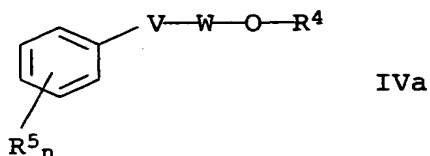
n is 0, 1, 2 or 3, and

R⁵ is C₁- to C₈-alkyl, C₁- to C₈-alkoxy, halogen, C₁- to C₄-haloalkyl, C₁- to C₄-haloalkoxy, phenyl, phenoxy, halophenyl, halophenoxy, carboxyl, C₂- to C₈-alkoxycarbonyl or cyano.

Preference is likewise given to compounds of the general formula IIIa

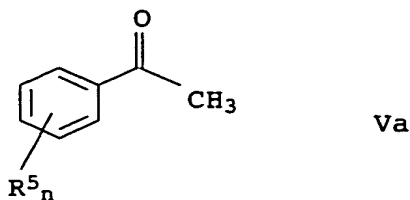


where n, V, W and R⁵ are as defined under the formula Ia or III, or of the general formula IVa



where n, V, W, R⁴ and R⁵ are as defined under the formula Ia or IIIa.

These compounds are prepared by employing as starting compound of the general formula V a compound of the general formula Va

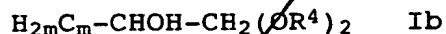


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where n and R⁵ are as defined under the formula Ia.

The process is furthermore particularly suitable for the preparation of compounds of the general formula Ib

5



Sub B3 } where m is a number from 1 to 10, and R⁴ is as defined in formula II, and for whose preparation use is made of a compound of the
10 general formula Vb



15 The process is very particularly suitable for the preparation of

- 2-phenyl-2,2-dimethoxyethanol,
2-phenyl-2,2-dimethoxyacetaldehyde and 2-phenylglyoxal
dimethyl acetal from methanol and acetophenone
- 20 - α-hydroxyoctanal dimethyl acetal from octanal and
- 2,2,3,3-tetramethoxypropanol from methylglyoxal dimethyl
acetal.
- 25 The auxiliary electrolyte present in the electrolysis solution is generally a halogen-containing auxiliary electrolyte, such as elemental halogen, an alkyl halide or a hydrogen halide. Halogen-containing salts, in particular iodides or bromides, can also preferably be employed. Examples are ammonium halides, such
30 as ammonium bromide, ammonium iodide and tetrabutylammonium iodide. Particularly preferred metal halides are furthermore alkali metal halides, such as sodium bromide, sodium iodide, potassium iodide and potassium bromide.
- 35 The metal salts (S) are preferably those derived from mineral acids. The anions of the metal salt are thus, for example, phosphate, sulfate, nitrate, perchlorate or halide.

The cations of the metal salt (S) are preferably iron, nickel,
40 platinum, palladium, cobalt, zinc, silver or copper ions. The metal salt (S) is generally added to the electrolysis solution in amounts such that its metal ions are present therein in amounts of from 1 to 1000 ppm by weight, preferably from 5 to 500 ppm by weight, particularly preferably from 5 to 300 ppm by weight,
45 based on the total amount of electrolysis liquid.

If desired, conventional co-solvents are added to the electrolysis liquid. These are the inert solvents having a high oxidation potential which are generally conventional in organic chemistry. Examples which may be mentioned are dimethyl carbonate
5 and propylene carbonate. Besides said co-solvents, water can also be added to the electrolysis liquid, although the water content should not exceed 5% by weight, based on the total amount of electrolysis liquid.

10 In general, the electrolysis liquid has the following composition:

- a starting compound of the general formula V
- 15 - an alcohol of the general formula II
- a halogen-containing auxiliary electrolyte
- catalytic amounts of the metal salt (S)
- 20 - possibly the desired products of the general formulae I, III and IV
- possibly other by-products of electrolysis which are derived
25 from the compounds of the general formulae I, II, III, IV and V
- if desired, other conventional co-solvents.

30 The ratio between the products of the general formulae I and V and the other by-products to the starting compounds in the electrolysis liquid and the ratio of the individual products having different degrees of oxidation to one another is of course, dependent on the progress of the reaction.

35 The ratio between the products of the general formulae I, III, IV and V and the other by-products to the starting compounds in the electrolysis liquid and the ratio of the individual products having different degrees of oxidation to one another is of course
40 dependent on the progress of the reaction.

In general, the amount of charge expended for the reaction is from 1 to 7 F per mole of starting compound of the general formula V. From 3.5 to 4 F are preferably employed if mixtures
45 are desired which are intended to contain, as principal components, compounds of the formulae I and III, and from 4.5 to 5.5 F are employed if mixtures are desired which are intended to

contain, as principal components, compounds of the formulae I and IV.

The process according to the invention can be carried out in all conventional types of electrolysis cell. Preference is given to undivided flow cells.

The current densities at which the process is carried out are generally from 0.5 to 25 A/dm². The temperatures are usually from -20 to 60°C, preferably from 0 to 60°C. The process is generally carried out at atmospheric pressure. Higher pressures are preferably used if higher temperatures are to be used in order to prevent the starting compounds or co-solvents from boiling.

15 Examples of suitable anode materials are noble metals such as platinum, or metal oxides, such as ruthenium or chromium oxide, or mixtures of the RuO_x/TiO_x type. Preference is given to graphite or carbon electrodes.

20 Suitable cathode materials are generally iron, steel, nickel, and noble metals, such as platinum and graphite and carbon materials.

When the reaction is complete, the electrolysis liquid is worked up by general separation methods. To this end, the electrolysis liquid is generally first distilled, and the individual compounds are obtained separately in the form of different fractions. Further purification can be carried out, for example, by crystallization or chromatography.

30 Experimental part

All experiments were carried out in an undivided cell having 11 bipolar electrodes (10 gaps, gap separation 1.5 mm).

35 Current density: 3.4 A/dm²

Flow rate: 400 l/h

Example 1:

40

Batch:

450 g of acetophenone
30 g of potassium iodide
2460 g of methanol
Fe(III): 5 ppm
steel 1.4301
graphite
7.03 h

45 Cathode:

Anode:

Duration:

5 Yields of the target products:

10 2-phenyl-2,2-dimethoxy acetate:	0%
Total:	66%

15 Batch:	450 g of acetophenone 30 g of potassium iodide 2460 g of methanol Fe(III): 5 ppm
Cathode:	Graphite
20 Anode:	Graphite
Duration:	7.03 h
Temperature:	36°C
Amount of charge:	3.5 F
Current strength:	5 A
25 Conversion:	84%

	2-phenyl-2,2-dimethoxyethanol:	15%
30	2-phenyl-2,2-dimethoxyacetaldehyde:	24%
	2-phenylglyoxal dimethyl acetal:	8%
	phenylglyoxylic acid methyl orthoester and methyl	
	2-phenyl-2,2-dimethoxy acetate:	3%
	Total:	50%

35

Batch:	450 g of acetophenone
	90 g of potassium iodide
40	2460 g of methanol
	Fe(III): 5 ppm
Cathode:	steel 1.4301
Anode:	graphite
Duration:	7.03 h
45 Temperature:	55-58°C
Amount of charge:	3.5 F
Current strength:	5 A

Conversion: 88%

Yields of the target products:

2-phenyl-2,2-dimethoxyethanol: 38%

2-phenyl-2,2-dimethoxyacetaldehyde: 19%

5 2-phenylglyoxal dimethyl acetal: 12%

phenylglyoxylic acid methyl orthoester and methyl

2-phenyl-2,2-dimethoxy acetate: 1%

Total: 70%

10 Example 4:

Batch: 450 g of acetophenone
90 g of potassium iodide
2460 g of methanol

15 Fe(III): 5 ppm

Cathode: steel 1.4301

Anode: graphite

Duration: 10.47 h

Temperature: 55-58°C

20 Amount of charge: 5.5 F

Current strength: 5 A

Conversion: >99%

Yields of the target products:

2-phenyl-2,2-dimethoxyethanol: 39%

25 2-phenyl-2,2-dimethoxyacetaldehyde: 0%

2-phenylglyoxal dimethyl acetal: 3%

phenylglyoxylic acid methyl orthoester and methyl

2-phenyl-2,2-dimethoxy acetate: 39%

30 Example 5:

Batch: 450 g of octanal
90 g of potassium iodide
2460 g of methanol

35 Fe(III): 5 ppm

Cathode: MKUS-F04 (SGL)

Anode: Graphite felt RVG 2003, 6 mm
(Deutsche Carbon)

Duration: 3.76 h

40 Temperature: 55-58°C

Amount of charge: 2 F

Current strength: 5 A

Conversion: >99%

Yield: 37% α -hydroxyoctanal dimethyl

45 acetal

Example 6:

Batch: 450 g of octanal
90 g of potassium iodide
2460 g of methanol
Fe(III): 5 ppm
MKUS-F04 (SGL)
Cathode: Graphite felt RVG 2003, 6 mm
Anode: (Deutsche Carbon)
3.76 h
10 Duration: 26-28°C
Temperature: 2 F
Amount of charge: 5 A
Current strength: 97%
Conversion: 45% α -hydroxyoctanal
15 Yield: dimethyl acetal

Example 7:

20 Batch: 450 g of methylglyoxal
dimethyl acetal
45 g of potassium iodide
2505 g of methanol
0.11 g NiSO₄
25 Cathode: graphite
Anode: graphite
Duration: 5 h
Temperature: 30°C
Current strength: 5 A
30 Conversion: 52%
Selectivity: 59.4%
Yield of 2,2,3,3-tetramethoxypropanol: 31%

Comparative Example 1:

35 Batch: 450 g of acetophenone
30 g of potassium iodide
2460 g of methanol
steel 1.4301
Cathode: 40 Anode: graphite
Duration: 7,03 h
Temperature: 36°C
Amount of charge: 3.5 F
Current strength: 5 A
45 Conversion: 98%
Yields of the target products:
2-phenyl-2,2-dimethoxyethanol: 19%

2-phenyl-2,2-dimethoxyacetaldehyde: 12%
2-phenylglyoxal dimethyl acetal: 5%
phenylglyoxylic acid methyl orthoester and methyl
2-phenyl-2,2-dimethoxy acetate: 9%
5 Total: 45%

Comparative Example 2:

10 Batch: 450 g of acetophenone
30 g of potassium iodide
2460 g of methanol
Cathode: graphite
Anode: graphite
Duration: 7.03 h
15 Temperature: 36°C
Amount of charge: 3.5 F
Current strength: 5 A
Conversion: 95%
Yields of the target products:
20 2-phenyl-2,2-dimethoxyethanol: 7%
2-phenyl-2,2-dimethoxyacetaldehyde: 25%
2-phenylglyoxal dimethyl acetal: 3%
phenylglyoxylic acid methyl orthoester and methyl
2-phenyl-2,2-dimethoxy acetate: 1%
25 Total: 36%

Comparative Example 3:

30 Batch: 450 g of octanal
90 g of potassium iodide
2460 g of methanol
Cathode: graphite
Anode: graphite
Duration: 3.76 h
35 Temperature: 55-58°C
Amount of charge: 2 F
Current strength: 5 A
Conversion: >99%
Yield: 30%
40

Comparative Example 4:

45 Batch: 450 g of octanal
90 g of potassium iodide
2460 g of methanol
Cathode: graphite
Anode: graphite

Duration:	3.76 h
Temperature:	26-28°C
Amount of charge:	2 F
Current strength:	5 A
5 Conversion:	>99%
Yield:	40%

Comparative Example 5:

10 Batch:	450 g of methylglyoxal dimethyl acetal 45 g of potassium iodide 2505 g of methanol
Cathode:	graphite
15 Anode:	graphite
Duration:	5 h
Temperature:	30°C
Current strength:	5 A
Conversion:	>99%
20 Selectivity:	24.6%
Yield:	24.6% 2,2,3,3-tetramethoxypropanol

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